

NUCLEAR MAGNETIC RESONANCE OF AN IRON-PYRIDINE CLATHRATE

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ABSTRACT

The wide line proton magnetic resonance study of solid iron-pyridine clathrate was carried out over the temperature range 77–415° K at 7.6 MHz. The crystal lattice was found to be rigid and non-rotating at 77° K. The data suggest some sort of protonic oscillation upto 330° K and an abrupt fall in the region 330–365° K. This has been attributed to the rotation of the molecule as a whole about the crystallographic symmetry axis through iron molecule. Above the transition region, the second moment increases upto the melting point which may be ascribed to the change in the crystalline structure due to the modification in the electronic field density of caged molecules. The activation energy for the motion was found 12.4 Kcal/mole approximately.

INTRODUCTION

BROAD line proton magnetic resonance spectra provide important information as to the intramolecular motion in the solid phase and the rate processes involved in molecular crystals. The present study reports the results of the investigations carried out on solid iron-pyridine clathrate.

EXPERIMENTS AND CALCULATIONS

(a) The NMR derivative spectra were recorded at 7.6 MHz on variable frequency broad line spectrometer model V-4200, using V-4340 variable temperature probe and 12 inch magnet system at Tata Institute of Fundamental Research, Bombay. The accuracy in the measurements is ± 1 Gauss². The high purity sample was obtained from Chemistry Department, Lucknow University.

(b) The theoretical rigid lattice proton, second moment consists of two parts, the intramolecular contribution S_1 and the intramolecular contribution S_2 . S_1 arises due to the interaction of the protons of the same molecule and this can be calculated from Van Vleck's theory¹ using Bearden and Watt's² values of physical constants,

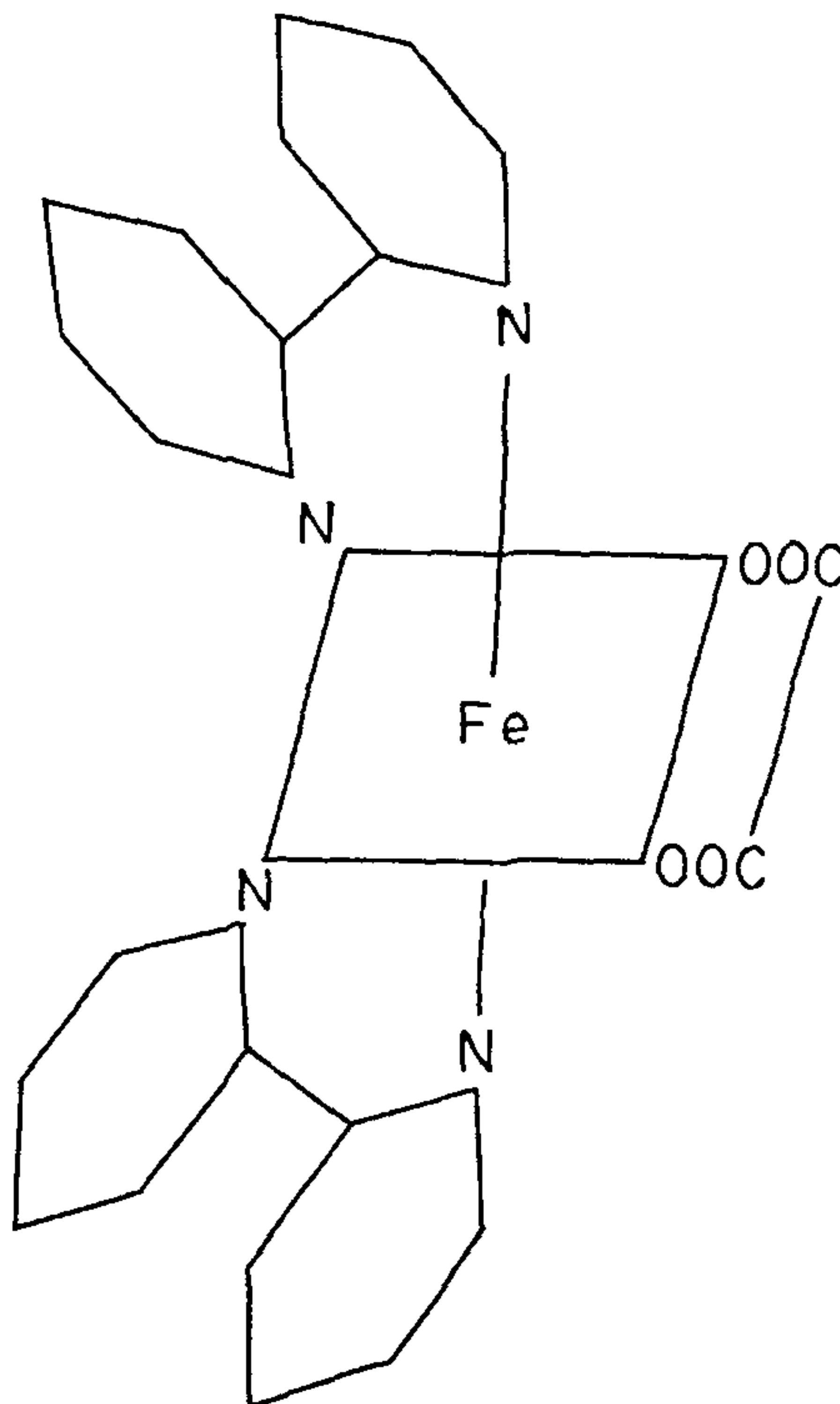
$$S_1 = 715.9/N \sum_{j < k} r_{jk} \text{ Gauss}^2$$

where N is the number of magnetic nuclei over which the summation is taken and r_{jk} is the distance between j th and k th nuclei. The value of intramolecular contribution comes out as 19.9 Gauss². The intramolecular contribution S_2 was obtained by the method of Andrew and Eades³ and the value was 6.9 Gauss². The total rigid lattice proton second moment, is $19.9 + 6.9 = 26.8$ Gauss².

(c) The experimental second moments were calculated from the trapezium rule⁴ applying a correction for the finite modulating field. The experimental second moment at 77° K was found to be 28.1 ± 1 Gauss².

DISCUSSION

The variation of the second moment with temperature is shown in figure 2. The experimental second moment at 77° K, fairly agrees with the theoretically calculated value of 26.8 Gauss². This shows that the lattice is rigid and non-rotating at



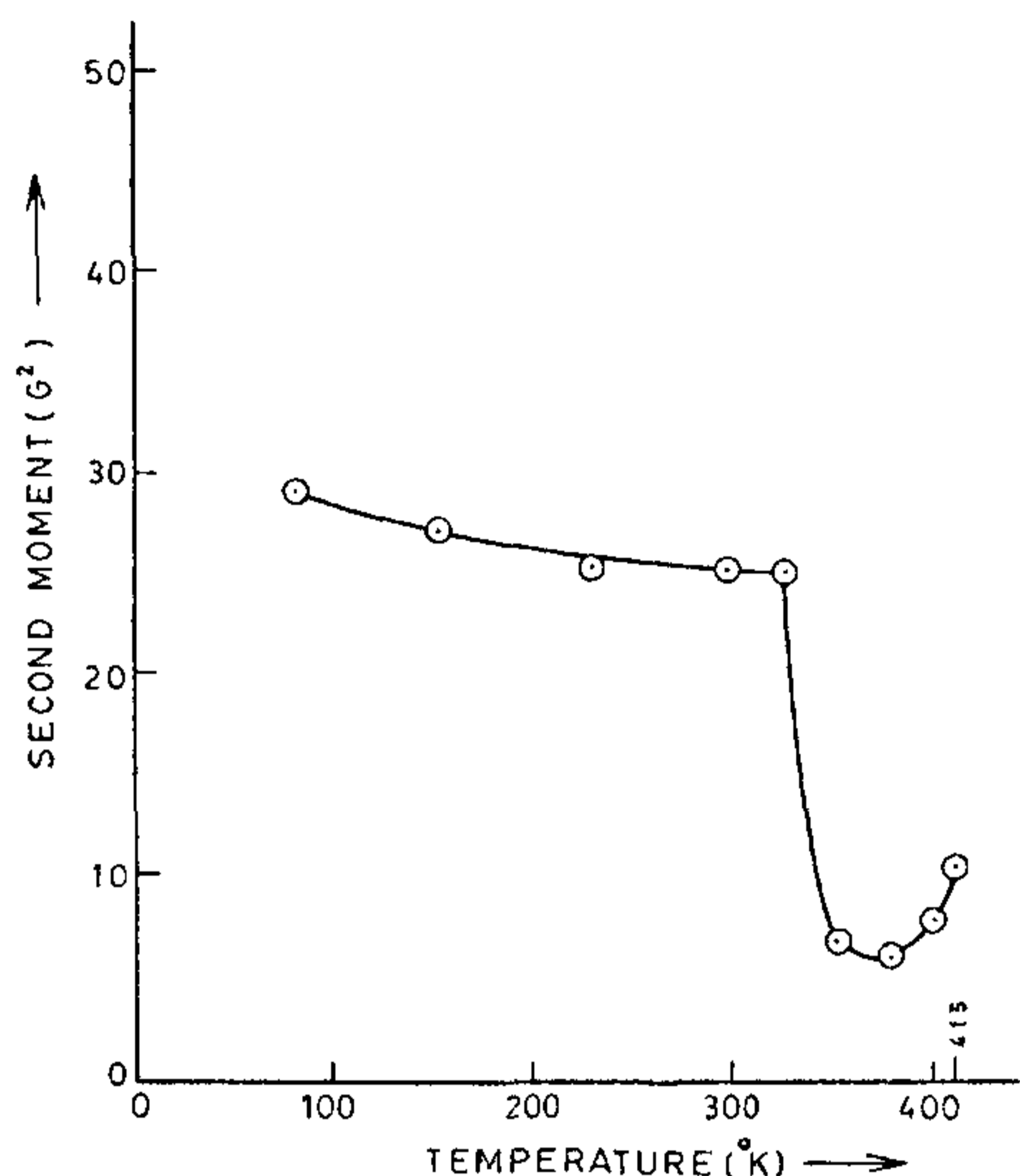


Figure 1, 2. 1. Molecular model of iron-pyridine clathrate, 2. Variation of second moment with temperature for iron-pyridine clathrate.

77° K. Above 77° K, the observed second moment decreases and has the value 24.0 Gauss² at 225° K. This reduction may be attributed to the presence of torsional oscillations in the solid iron-pyridine clathrate (figure 1). The further sharp fall suggests the onset of some type of motion. Considering the rotation of the whole molecule to be the cause of the observed reduction, the reduction due to this motion can be computed by using the method of Gutowsky and Pake⁵. The intramolecular contribution in such cases is reduced by a factor

$$\frac{1}{4} \left[\frac{3 \cos^2 r_{jk}}{2} - 1 \right]^2$$

where r_{jk} is the angle made by the line joining the j th and k th proton with the axis of rotation. The intramolecular contribution⁶ is shown to be reduced by a factor 0.24. The calculations for the molecular rotation, as a whole, yielded a value of 8.8 Gauss² at 385° K and support the possibility of molecular reorientation.

Increasing the temperature above 385° K, the second moment unusually increases upto the melting point, suggesting some change in the crystalline structure. This probably is caused by the modification in the electronic field density of caged molecules due to molecular rotation.

SECOND MOMENT OF TRAPPED MOLECULES

The second moment of the trapped molecules⁷ can be obtained, in principle, from the complex signal. The second moment of the trapped molecules S_{MOL} is to be expressed by the relation,

$$S_{\text{MOL}} = S_{\text{intra}} + S_{\text{cage}} + S_{\text{mol}}$$

where S_{intra} is the intramolecular contribution from the trapped molecule, S_{cage} , the contribution from the magnetic nuclei in the cage lattice and S_{mol} is that from the trapped molecule (figure 1) S_{intra} can be obtained by knowing the structure and motion of the trapped molecule. S_{cage} is calculated from the cage lattice structure and the relative position of the trapped molecules inside it. S_{mol} is determined from the relative position of the molecule in the cage lattice but is not usually known with certainty.

From the experimental curves at 77° K and 295° K, $S_{\text{MOL}}(77^\circ \text{K})$ and $S_{\text{MOL}}(295^\circ \text{K})$ are compared below, for expected intramolecular values at two states, i.e., $S_{\text{intra}}(\text{static})$ and $S_{\text{intra}}(\text{motion})$ representing the static configuration and a state with certain degree of motion:

S_{MOL} 77° K	S_{intra} static	S_{MOL} 295° K	S_{intra} motion
4.8 + 2	2.5	3.8 ± .5	2.5

However, for 2,2'-dipyridyl⁸ the intramolecular contribution S_i is 6.24 Gauss² and S_c , the intramolecular contribution is 1.57 Gauss².

ACTIVATION ENERGY

The motion of an organic molecule in its own crystal is hindered by a potential barrier built up by the neighbouring molecules of the same kind. In the present case the corresponding barrier height for the intramolecular rotation can be obtained by using an equation given earlier^{9,10},

$$\Delta H^2 = B^2 + (C^2 - B^2) \frac{2}{\pi} \tan^{-1} \left[\frac{\alpha \gamma \Delta H}{2 \pi \nu_i} \right]$$

which is connected with the following relation,

$$\nu_i = \nu_0 \exp(-E_A / RT)$$

where symbols have their usual meanings. The plot of $\log \nu_i$ versus $1/T$ yields a straight line. Its slope multiplied by the gas constant R gives the value of the activation energy. The value was found to be roughly equal to 12.4 Kcal/mol. Waugh and Fedin's Theory yielded a value of 13.5 Kcal/mol. This value would be

only approximate due to the fewer observations in the first transition region.

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GROWTH RATE OF CALCITE CONCRETIONS

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ABSTRACT

Growth rates of two calcite concretions are calculated using a mathematical model and radiocarbon ages. The rates are within the range observed by earlier workers. Stable carbon isotope compositions of the nodules indicate precipitation under equilibrium with atmospheric carbon dioxide.

INTRODUCTION

CALCITIC concretions generally grow from supersaturated solutions often nucleating around a central body. Although it is realised that they grow very slowly in natural systems, their growth mechanism is still not quite certain. One process operative is probably diffusion controlled. Very few attempts have been made to experimentally measure the growth rates, perhaps due to the non-availability of suitable samples. This paper describes growth studies, using radiocarbon ages, on two calcitic concretions from a lake in Rajasthan, North Western India. The lake, Naliasar (75° 10' E, 26° 55' N), measuring about 4 km long and 2 km wide is one of the few freshwater lakes in the region. It lies very close to Sambhar, a large brackish lake. Naliasar gets filled during monsoon but remains as a playa for most other parts of the year. The lake sediments have in them concretions of several sizes. Two nearly spherical nodules containing more than 90% calcium carbonate, from depths of 5 cm and 12 cm respectively were collected for the present study.

MATERIALS AND METHODS

Since it was difficult to obtain layer-wise samples,

TABLE I

Experimental and model-derived parameters of the calcite nodules

Fraction details	Equivalent radius in cm	¹⁴ C age in yrs* b.p. (<i>t</i> _{1/2} = 5730 yrs)	Growth rate in μm/10 ³ yrs	† ¹³ C‰ δ vs. PDB
<i>Sample No. PRL-358 (depth below surface: 5 cm)</i>				
Outer shell	1.81 (R ₂)	13120 ± 190	1745	+ 2.33
Inner core	1.61 (R ₁)	16030 ± 240		+ 2.65
<i>Sample No. PRL-359 (depth below surface: 12 cm)</i>				
Outer shell	1.981 (R ₃)	16010 ± 380	1600	+ 2.54
Middle shell	1.902 (R ₂)	20580 ± 580	812	+ 2.96
Inner core	1.104 (R ₁)	22980 ± 460	3100	+ 3.30

* Quoted with 1 sigma error. b.p. = before present.

† $\delta^{13}\text{C}\text{‰} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3$ where $R = \delta^{13}\text{C}/12\text{C}$.